

FORM PTO-1390 (Modified)  
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

14283 (SIL 0034)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

09/806209

INTERNATIONAL APPLICATION NO.  
PCTUS99/22490

INTERNATIONAL FILING DATE  
27 September 1999 (27.09.99)

PRIORITY DATE CLAIMED  
28 September 1998 (28.09.98)

TITLE OF INVENTION

**ORGANOSILOXANE CONTAINING MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS**

APPLICANT(S) FOR DO/EO/US

**George A. Policello, Anna Czech and Jack Burgazi**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- ☒ A copy of the International Search Report (PCT/ISA/210).
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
- ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
- ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 20 below concern document(s) or information included:**

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

**Courtesy copy of International Application**

**Assignee: Crompton Corporation**

**Assignee Address: Middlebury, CT 06749**

|  |                               |                          |
|--|-------------------------------|--------------------------|
| U.S. APPLICATION NO. (IF KNOWN, SEE 37 C.F.R. 1.5) | INTERNATIONAL APPLICATION NO. | ATTORNEY'S DOCKET NUMBER |
| 09/806209  | PCT/US99/22490                | 14283(SIL 0034)          |

21. The following fees are submitted:

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :**

- |                                     |   |                   |
|-------------------------------------|---|-------------------|
| <input type="checkbox"/>            | Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . | <b>\$1,000.00</b> |
| <input checked="" type="checkbox"/> | International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . .   | <b>\$860.00</b>   |
| <input type="checkbox"/>            | International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . .  | <b>\$710.00</b>   |
| <input type="checkbox"/>            | International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . .   | <b>\$690.00</b>   |
| <input type="checkbox"/>            | International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . .   | <b>\$100.00</b>   |

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

**\$860.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

**\$130.00**

| CLAIMS             | NUMBER FILED | NUMBER EXTRA | RATE      |        |  |
|--------------------|--------------|--------------|-----------|--------|--|
| Total claims       | 10 - 20 =    | 0            | x \$18.00 | \$0.00 |  |
| Independent claims | 3 - 3 =      | 0            | x \$80.00 | \$0.00 |  |

Multiple Dependent Claims (check if applicable).

**\$0.00**

**TOTAL OF ABOVE CALCULATIONS =**

**\$990.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

**\$0.00**

**SUBTOTAL =**

**\$990.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

**\$0.00**

**TOTAL NATIONAL FEE** =

**\$990.00**

**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).**

**\$0.00**

**TOTAL FEES ENCLOSED** =

**\$990.00**

|                           |    |
|---------------------------|----|
| Amount to be:<br>refunded | \$ |
| charged                   | \$ |

 A check in the amount of \_\_\_\_\_ to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **23-2656** in the amount of **\$990.00** to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **23-2656** A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

**SEND ALL CORRESPONDENCE TO:**

**Edward W. Grolz**  
**SCULLY, SCOTT, MURPHY & PRESSER**  
**400 GARDEN CITY PLAZA**  
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SIGNATURE

Edward W. Grolz

NAME \_\_\_\_\_

**33,705**

REGISTRATION NUMBER

**March 27, 2001**

DATE \_\_\_\_\_

09/806209

**CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)**

IC08/Rec'd PCT Doc No. 2.7 MAR 2001

Applicant(s): George A. Policello, Anna Czech and Jack Burgazl

14283

|                          |                         |                        |                              |
|--------------------------|-------------------------|------------------------|------------------------------|
| Serial No.<br>Unassigned | Filing Date<br>Herewith | Examiner<br>Unassigned | Group Art Unit<br>Unassigned |
|--------------------------|-------------------------|------------------------|------------------------------|

Invention: **ORGANOSILOXANE CONTAINING MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS**

I hereby certify that the following correspondence:

**NEW PCT APPLICATION***(Identify type of correspondence)*

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under

37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231

**March 27, 2001***(Date)***Mishelle Mustafa***(Typed or Printed Name of Person Mailing Correspondence)**(Signature of Person Mailing Correspondence)***EL 835917801 US***("Express Mail" Mailing Label Number)***Note: Each paper must have its own certificate of mailing.**

## Organosiloxane Containing Modified Groups in Pesticidal Compositions

### Background of the Invention

5 Many pesticides require the addition of an adjuvant to the spray mixture to provide wetting and spreading on foliar surfaces. Often that adjuvant is a surfactant, which can perform a variety of functions, such as increasing spray droplet retention on difficult to wet leaf surfaces, or to provide penetration of the herbicide into the plant cuticle. These adjuvants are provided either as a  
10 tankside additive or used as a component in pesticide formulations.

Gaskin, *et al.*, (*Pestic. Sci.* 1993, 38, 185-192) demonstrated that some trisiloxane ethoxylates (TSE), such as Silwet L-77® surfactant (available from Witco Corp. of Greenwich, CT), can antagonize cuticular penetration of a herbicide into grasses, when compared to the herbicide alone. The term  
15 antagonism is used to indicate that the treatment of herbicide plus adjuvant is less effective than the comparative herbicide treatment.

Sandbrink, *et al.*, (*Pest. Sci.* 1993, 38, 272-273) published that a TSE antagonized glyphosate performance relative to glyphosate alone in the control of *Panicum maximum* Jacq. Snow, *et. al.*, *Langmuir*, 1993, 9, 424-30, discusses the  
20 physical properties and synthesis of novel cationic siloxane surfactants. These siloxanes are based on the reaction of a chloropropyl modified trisiloxane with an alkanolamine, such as N-methylethanolamine, which was further reacted with a halide to make a quaternary surfactant.

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Petroff, *et al.*, (EP 92116658) describes the use of cationic, quaternary trisiloxanes to enhance the efficacy of glyphosate on velvetleaf, a broadleaf weed. Henning, *et al.*, (DE4318537) describes cationic siloxanyl modified polyhydroxy hydrocarbon or carbohydrate for use with plant protection agents. These  
5 compounds are derived from a saccharide containing 1 to 10 pentose and/or hexose units, modified with a quaternary ammonium group, and a siloxane moiety. Reid, *et al.*, (USP 3,389,160) describes amino modified siloxane alkoxylates where the amino functionality appears as the terminal group on the alkyleneoxide moiety, opposite the siloxane group. Policello in PCT WO  
10 97/32475 discloses amino modified siloxanes wherein the amine is bound by an ether bond to the siloxane backbone wherein the amine may be terminal or pendant to the backbone.

Dietz et al. in US Patent No. 5,891,977 describes organopolysiloxanes comprising polyhydroxyorganyl radicals and polyalkylene radicals, their process  
15 and use. Specifically these materials are describes as being useful in coatings, paints and inks, as well as emulsifiers for water-in-oil and oil-in-water systems, such as hair care formulations. Although these materials are mentioned as being practical for many applications, these were not shown to have utility as adjuvants for pesticidal applications.

20

### Summary of the Invention

Organosiloxanes for use with pesticidally active compositions and those with utility in pesticide formulations to treat plants and animals are those

substituted with at least one aminealkoxylate group, which are novel siloxane structures. Intermediates for the manufacture for said siloxane are also disclosed herein.

## 5 Detailed Description of the Invention

The amino alkoxylate organosiloxanes described herein are useful as adjuvants for pesticide formulations, including but not limited to applications which may be used to treat plants or animals. The pesticidal formulations include (a) at least one modified organosiloxane; and (b) at least one pesticidally active component, but may contain optional ingredients.

### (A) ORGANOSILOXANES

Preferably, the modified organosiloxanes of the present invention have the average general formula:



wherein f is between 0 to 50, preferably 1 to 5, more preferably 1 to 2, most preferably 1, d = 0 to 2, most preferably 0, e = 0 to 3, most preferably 0, if the siloxane is not cyclic, g = 2 + e + 2d, and if the siloxane is cyclic g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an amino alkoxylate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, preferably 2 to 3, each b is 2 to 15, preferably 2 to 8, each B is a divalent bridging group of C1 to C8, preferably C3 to C4, each optionally OH substituted, z = 0 to 1, preferably 0, R<sup>1</sup> is

hydrogen or a hydrocarbon radical of 1 to 4 carbons,  $R^2$  is either a polyether of the structure  $-BO(C_aH_{2a}O)_cR^1$ , hydrogen, an alkyl radical containing 1 to 18 carbons, preferably methyl,  $c$  is 0 to 15, and  $T$  is a univalent organic moiety.

Preferably most  $R^2$  groups are methyl, but some may be polyethers of the structure  $-B(C_aH_{2a}O)_bR^1$  as defined above, e.g.,  $-C_3H_6(C_2H_4O)_8OH$  and  $-C_3H_6(C_2H_4O)_6(C_3H_6O)_2OCH_3$ . Exemplary  $B$  are  $-(CH_2)_2-$ ,  $-(CH_2)_3-$ , and  $-CH_2CH(OH)CH_2-$  and  $-CH_2C_6H_9(OH)CH_2-$ . Examples of  $R^1$  are  $-H$ , and  $-CH_3$ . Most preferably all  $Q$  groups which are terminal are methyl and there is at least one amino alkoxyate pendant, though alternatively, the terminal groups may be amino alkoxyates and the pendant  $Q$  groups may all be methyl. A particularly preferred siloxane is a  $(CH_3)_3SiOSiCH_3(Q)OSi(CH_3)_3$  wherein the  $Q$  is an amino alkoxyate.

Preferably  $a$  is such that there is a mixture of ethylene oxide (EO), propylene oxide (PO) units and butylene oxide (BO) units. Preferably, for aqueous applications, there is a preponderance of EO units, most preferably every  $a = 2$ . For non-aqueous applications, such as crop oil concentrates, there may be more PO and BO units. When  $Q$  contains a mixture of oxyalkylenes, it may be blocked or random. One skilled in the art will understand the advantages in the position of the oxyethylene relative to the oxypropylene, when the alkyleneoxide group is blocked.

$T$  groups preferably are alkyls (which may be branched, linear or cyclic) of less than 8 carbons. Another preferred  $T$  is an alkyl amine functionality,  $-BNR^2_2$ , which may be further substituted (e.g., with an alkyl) or be further alkoxyated,

e.g.,  $-\text{BN}(\text{C}_a\text{H}_{2a}\text{O})_c\text{R}^1$ . Alternatively, T may be an amino alkyl siloxane or an amino alkyl hydroxy siloxane, e.g.,  $-\text{B-N-B}-(\text{SiO}_{1/2}\text{R}^6)-\text{X}^1$  wherein  $\text{X}^1$  is a siloxane per formula I above (with the  $-\text{B-N-B}-(\text{SiO}_{1/2}\text{R}^6)-\text{X}^1$  group being taken as  $[\text{O}_{1/2}\text{MeSi}(\text{Q})\text{O}_{1/2}]$  or  $[\text{O}_{1/2}\text{SiMe}_2\text{Q}]$ ) and  $\text{R}^6$  is  $\text{O}_{1/2}$  or  $-\text{CH}_3$ . If T contains a siloxane, it

5 preferably is the same backbone as the siloxane to which Q is attached.

The Q groups may include protonated amines, *i.e.*, where there is a hydrogen ion attached to the nitrogen in the Q group, which can occur to the aminosilicone alkoxylates under acidic conditions. Also contemplated herein are quaternary versions of Q, *i.e.*, where there is a third T group on the nitrogen in

10 Q, but said quaternary compounds are not preferred for use in the present invention since they would tend to be phytotoxic.

Preferred Q structures are wherein  $\text{R}^1$  is hydrogen or methyl, a is 2, and b is from 4 to 6. Specific Q groups are  $-\text{C}_2\text{H}_4\text{N}[\text{C}_2\text{H}_4\text{O}(\text{EO})_5\text{CH}_3]_2$ ;  
 $-\text{C}_2\text{H}_4\text{N}[\text{C}_2\text{H}_4\text{O}(\text{EO})_5\text{H}]_2$ ;  $-\text{C}_3\text{H}_6\text{N}[\text{C}_3\text{H}_6\text{O}(\text{EO})_3(\text{PO})_2\text{H}](\text{C}_2\text{H}_5)$ ;  
 15  $-\text{C}_3\text{H}_6\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}[\text{C}_2\text{H}_4\text{O}(\text{EO})_6\text{H}]_2$ ;  
 $-\text{C}_3\text{H}_6\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}[\text{C}_3\text{H}_6\text{O}(\text{EO})_6\text{H}]$ ;  $-\text{C}_3\text{H}_6\text{C}(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)[\text{C}_3\text{H}_6\text{O}(\text{PO})_5\text{H}]$ ;  
 $-\text{C}_3\text{H}_6\text{OCH}_2(\text{OH})\text{CH}_2\text{NHC}_3\text{H}_6\text{O}(\text{EO})_2\text{CH}_2\text{CH}(\text{CH}_3)\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OC}_3\text{H}_6\text{SiO}_{2/2}((\text{CH}_3)_3\text{SiO}_{1/2})_2$ ;  
 and  $-\text{C}_3\text{H}_6\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}[\text{CH}_2\text{CH}_2\text{O}(\text{EO})_4\text{H}]_2$ .

Preferred aminosilicone alkoxylates are trisiloxanes with  $\text{R}^5$  being methyl, with

20 B preferably being a C1 to C4 alkylene, most preferably propylene or 2-hydroxy propylene.



PESTICIDES

The pesticidal compositions of the present invention also include at least one pesticide, especially acid functionalized ones, i.e., compounds that contain at least one carboxylic, sulfonic or phosphonic acid group or their salt or ester. The term pesticide means any compound used to destroy pests, e.g., rodenticides, fungicides, and herbicides. Illustrative examples of pesticides which can be employed include, but are not limited to, growth regulators, photosynthesis inhibitors, pigment inhibitors, mitotic disrupters, lipid biosynthesis inhibitors, cell wall inhibitors, and cell membrane disrupters. The amount of pesticide employed in compositions of the invention varies with the type of pesticide employed. More specific examples of pesticide compounds that can be used with the compositions of the invention are: phenoxy acetic acids, phenoxy propionic acids, phenoxy butyric acids, benzoic acids, triazines and s-triazines, substituted ureas, uracils, bentazon, desmedipham, methazole, phenmedipham, pyridate, amitrole, clomazone, fluridone, norflurazone, dinitroanilines, isopropalin, oryzalin, pendimethalin, prodiamine, trifluralin, glyphosate, sulfonylureas, imidazolinones, clethodim, diclofop-methyl, fenoxaprop-ethyl, fluazifop-p-butyl, haloxyfop-methyl, quizalofop, sethoxydim, dichlobenil, isoxaben, and bipyridylium compounds.

The pesticide may be a liquid or a solid. If a solid, it is preferable that it is soluble in a solvent prior to application, and the silicone may act as a surfactant for such solubility or additional surfactants may perform this function.

It is preferable that the pesticide be one that is other than a solvent. For example, it is preferable that the pesticide do not include solvents which have also at times been categorized as being pesticidally active compounds. Such solvents include paraffinics; oils including animal, mineral, vegetable, silicone, and so forth; fatty acids, esters, and amides of fatty acids; alkanes; ketones; alcohols; glycols; alkyl/aryl alkoxylates; diols; acetates; and so forth.

### EXCIPIENTS

Buffers, preservatives and other standard excipients known in the art also may be included in the composition. When the compositions of the present are insoluble in distilled water, spreading may be achieved by the addition of a small amount of an acid, such as acetic acid, to protonate the amine functionality, thereby increasing water solubility.

Solvents may also be included in compositions of the present invention. These solvents are in a liquid state at room temperature. Examples include water, alcohols, aromatic solvents, oils (i.e. mineral oil, vegetable oil, silicone oil, and so forth), lower alkyl esters of vegetable oils, fatty acids, ketones, glycols, polyethylene glycols, diols, paraffinics, and so forth. Particular solvents would be 2, 2, 4-trimethyl, 1-3-pentane diol and alkoxylated (especially ethoxylated) versions thereof, See US Patent No. 5,674,832 to Keyes, or n-methyl-pyrrolidone.

Moreover, other cosurfactants, which have short chain hydrophobes which do not interfere with superspreading may be included. See US Patent No. 5,558,806 to Policello et al., which is incorporated by reference.

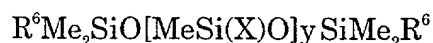
The cosurfactants useful herein include nonionic, cationic, anionic, 5 amphoteric, zwitterionic, polymeric surfactants, or any mixture thereof. Surfactants are typically hydrocarbon based, silicone based or fluorocarbon based.

Useful surfactants include alkoxylates, especially ethoxylates, containing block copolymers including copolymers of ethylene oxide, propylene oxide, 10 butylene oxide, and mixtures thereof; alkylarylalkoxylates, especially ethoxylates or propoxylates and their derivatives including alkyl phenol ethoxylate; arylarylalkoxylates, especially ethoxylates or propoxylates. and their derivatives; amine alkoxylates, especially amine ethoxylates; fatty acid alkoxylates; fatty alcohol alkoxylates; alkyl sulfonates; alkyl benzene and alkyl 15 naphthalene sulfonates; sulfated fatty alcohols, amines or acid amides; acid esters of sodium isethionate; esters of sodium sulfosuccinate; sulfated or sulfonated fatty acid esters; petroleum sulfonates; N-acyl sarcosinates; alkyl polyglycosides; alkyl ethoxylated amines; and so forth.

Specific examples include alkyl acetylenic diols (SURFONYL- Air 20 Products), pyrrolidone based surfactants (e.g., SURFADONE – LP 100 – ISP), 2-ethyl hexyl sulfate, isodecyl alcohol ethoxylates (e.g., RHODASURF DA 530 – Rhodia), ethylene diamine alkoxylates (TETRONICS – BASF), and ethylene

oxide/propylene oxide copolymers (PLURONICS – BASF) and Gemini type surfactants (Rhodia).

Preferred surfactants include ethylene oxide/propylene oxide copolymers (EO/PO); amine ethoxylates; sorbitol ethoxylates; and so forth. The optional  
 5 silicone surfactants include trisiloxane alkoxyates (TSAs) of the general formula:



wherein  $y = 0$  to  $2$ , preferably  $1$ ,  $X$  is as above, and  $R^6$  is  $G$ , or an alkyl of one to four carbons. The preferred nonionic siloxane alkoxyates are trisiloxane  
 10 alkoxyates, where  $y = 1$ ,  $a = 3$ ,  $q = 4$  to  $8$ ,  $r = 0$ ,  $R^6$  is  $Me$ ,  $R^3$  is  $H$  or  $Me$ .

A suspension aid is preferably utilized if a pesticide concentrates is made with the modified siloxanes to improve physical stability.

#### MANUFACTURE OF SILOXANES

15 The amine modified organosiloxanes of the present invention may be made by the hydrosilation of a hydridosiloxane with an epoxy intermediate, such as allyl glycidal ether, vinyl cyclohexene monoxide, or an epoxy terminated allyl polyalkyleneoxide, followed by ring opening the epoxide with the appropriate amino alkoxyate group. The hydridosiloxanes described are commercially  
 20 available and may be made as known in the art. Hydrosilation conditions depend on the reactants, but are within the general conditions taught in Marciniac (*Comprehensive Handbook of Hydrosilylation*, Edited by Bogdan Marciniac, Pergamon Press).

5 oxides.

the siloxanes, thus, it is preferable to use with diamines siloxanes with only one epoxy functionality per molecule. The resulting product would be two siloxane chains linked by an amino alkoxylate amino bridge. Short chain siloxanes, e.g., trisiloxanes would be preferable for same.

15 the reaction product of an allyl or methallyl chloride and an alkoxyated amine compound and hydrosilate this allylic polyhydric amine onto hydridosiloxanes. Hydrosilation conditions depend on the amine and siloxane, but again are within the general conditions taught in Marciniak.

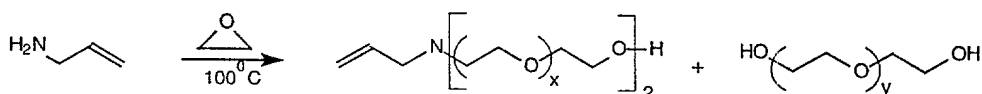
20 hydrosilated onto the backbone (e.g., an amino alkoxyate, polyether siloxane)  
such hydrosilations may be done sequentially or at the same time depending  
upon the reactivities of the species to be hydrosilated, as well as the desired end-

product. The reaction conditions for hydrosilating an allyl started polyether are well known in the art.

The alkenylamino polyalkyleneoxides intermediate structures to be reacted with the hydridosiloxanes are of the formula  $B'N[BO(C_aH_{2a}O)_bR^1]_{2-z}T_z$  wherein all formulae as are above, except B' is an alkenyl, with an  $\alpha, \beta$  unsaturation at the end of the alkenyl opposite from the nitrogen atom. The alkenyl could be C1-C18, preferably C1-C6, and most preferably allyl or methallyl. To make this alkenyl amine alkoxyate, an alkenyl salt, e.g., allyl bromide, is reacted with ammonia, or a secondary or primary amine. This amine product then is alkoxyated.

An exemplary alkoxylation procedure would be as follows (with chemistry noted below)- Charge allyl amine to reactor. Degas and pressurize with nitrogen. Heat to 105°C, and then add 25 psig (.0015 N<sup>2</sup>/m) of nitrogen above the pressure exerted by allyl amine. Gradually add EO, to maintain temperature below 115 C, and pressure below 80 psig (.0095 N<sup>2</sup>/m). The formation of the tertiary amine will cause a great drop in the reactor pressure, at this time continual addition of EO could proceed at 105-110°C and a pressure range of 60 - 80 psig (0.0066 to 0.0095 N<sup>2</sup>/m). After the required amounts of EO is added, the reaction is allowed to digest for 30 minutes, residual EO is removed by vacuum, the reactor is cooled, and the product removed by slight pressurization of the reactor.

Any glycol's which may have been produced due to utilization of a partially wet amine may be stripped by vacuum.



The allyl amino polyalkyleneoxides also may be prepared by reaction of an allyl glycidyl ether (or similar unsaturated epoxide) with an amine alkoxylate (which result in an ether bond). If a diamine is used for such a reaction, a diallylic speices will be formed, which will act as a crosslinker and prefereably should be used with a mon-hydridosiloxane. An alternative method uses aziridine, which is not preferred for toxicity reasons, are disclosed in PCT US97/04128, which is incorporated herein by reference.

The nonionic siloxane and the pesticides are commercially available and their manufacture is known in the art.

## USE

The modified organosiloxanes may be used in agricultural applications as adjuvants for pesticides wherein the siloxane is applied in a pesticide formulation to agricultural products or to treat animals. The composition of the present invention is useful as a tank side additive in an animal shampoo, or as a component in a herbicide formulation. In addition the compositions of the present invention are useful as adjuvants for other pesticides, such as, fungicides, insecticides, plant growth regulators, acaracides and the like. The pesticide formulations may be wet, dry, slurries or other formulations as are known in the art.

The siloxanes are added directly to a spray tank along with an acid functional pesticide, or as part of a pesticide formulation. When used as a tankside additive, the siloxane is present at weight concentrations between 0.001% and 5.0%, preferably between 0.025% and 0.5%. Likewise, when the modified organosiloxanes are used in a pesticide formulation (In-can), they are present at weight concentrations that will deliver between 0.001% and 5.0% to the final use dilution, preferably between 0.025% and 0.5%, of the final use dilution.

It is noted that most dilutions will be made with water, but in the case of crop oil concentrates, oils (mineral, silicone, animal or vegetable oils) will be the diluents.

When the compositions of the present invention are used in conjunction with a TSA, the weight ratio of the TSA to the modified organosiloxanes is between 5:95 and 95:5, preferably between 5:95 and 40:60. The blend may be accomplished by mixing physically the two components prior to use, or by adding them separately to a spray mixture at the point of use.

When the compositions of the present invention are used in conjunction with nonsilicone surfactants, the weight ratio of the nonsilicone surfactant to the modified organosiloxane is between 1:99 and 99:1, preferably between 99:1 and 40:60.

Additionally, the amino alkoxylate organosiloxanes also may be used generally as surface active agents in aqueous formulation where there is an acid functionalized component. These organosiloxanes also may be used as surface



active agents, including, but not limited to, as surfactants, wetting agents and softeners for textiles, flow and leveling agents in coatings, hair care products, skin care and creams for personal care applications and anti-static agents, detergents and softeners for laundry products.

5

### Examples

Unless otherwise indicated, all parts and percentages are by weight, and are based on the weight at the particular stage of the processing being described.

#### Example 1 - Alkoxylation of Allyl Amine

To a two liter Parr pressure reactor was charged 200.4 g of allyl mine. The reactor was heated to 60°C, which resulted in a pressure of 10 psig. To the system was added 25 psig of nitrogen, and 50 g of EO. The reactor was heated  
10 gradually until an exotherm was noticed. This occurred at 103°C and caused a pressure jump to 105 psig. After the reaction subsided the temperature was kept at 103 and more EO added between 40 - 60 psig. After approximately 100 g was added another exotherm occurred to 130°C and caused a raise in pressure to 70 psig. After this exotherm subsided the reaction behaved very well and  
15 continuous addition of EO was possible. Catalysis after the formation of a tertiary amine was not required for subsequent addition of EO. The temperature range of the reaction was 103 -110°C, with a pressure of range of 40 - 45 psig (including 25 psi of Nitrogen), and a rate of addition of 20-25 g/min. of EO.

Example 2

Aminosilicone alkoxylates were prepared by the slow addition of the desired allylamino polyalkyleneoxide to a reaction vessel containing heptamethyltrisiloxane (in a 1.3:1 mole ratio). Therefore, 25.7g of

5 heptamethyltrisiloxane (0.1155 moles), 39.3g of allylamine ethoxylate, 4.6 EO, (0.1501 moles), along with 30 g isopropanol (solvent) were weighed into a 250 mL roundbottom flask equipped with an addition funnel, reflux condenser and an overhead stirrer. The flask contents were heated to 65°C and catalyzed with 0.3 g of potassium trichloro-ethylene platinate (III) solution (1% in isopropanol) and

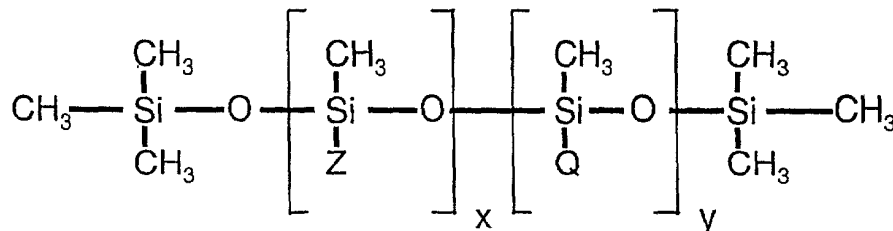
10 held at this temperature for 6 h. The reaction mixture was heated to 75 °C , and an additional 0.56 g of catalyst solution was added. The reaction mixture was maintained at this temperature for an additional 5 hours at which time another 0.26 g of catalyst solution was added to the reaction mixture, and stirred for an additional hour. The reaction was monitored by introducing a sample of the

15 reaction mixture into a fermentation tube containing KOH/water/ethanol solution. The generation of hydrogen indicates an incomplete reaction. The flask contents were mixed until the SiH intermediate was consumed. The mixture was cooled to 45 °C, filtered through a fine filter pad, and stripped on a Rotovap for 1.5 hours at 70°C and 1.0 mm Hg to yield a dark amber colored

20 product with a viscosity of 78 cps (Spindle LV-3 @ 100 rpm), a refractive index of 1.4520 (25°C) and an aqueous surface tension of 21.1 mN/m (0.1 wt%, Wilhelmy Plate). The resulting aminosilicone alkoxylate is shown in Table 1.

Table 1

## Description of Modified Organosiloxanes



5

| Reference | x | y | Description   |
|-----------|---|---|---|
| MSIL-1    | 0 | 1 | $\text{Q} = \text{C}_2\text{H}_4\text{N}[(\text{C}_2\text{H}_4\text{O})_a\text{H}_3]_2$ , where $a = 4.6$ |

## Example 3

10 This example demonstrates the utility of the organosilicone composition of the present invention as a surfactant. Aqueous solutions of this siloxane provided a significant reduction in surface tension relative to water. Surface tension was measured using a Cahn microbalance, with a sand blasted platinum blade as the sensor. Solutions of the various components were prepared at 0.1

15 wt% in 0.005M NaCl water (Deionized), as an equilibrium aid.

Spreading was determined by applying a 10  $\mu\text{L}$  droplet of surfactant solution to a polyester film (3M, IR 1140 transparency film) and measuring the spread diameter after 30 seconds. The solution was applied with an automatic pipette to provide droplets of reproducible volume. Deionized water that was

further purified with a Millipore filtration system was used to prepare the surfactant solutions.

**Table 2 - Comparison of Aqueous Surface Tension Properties**

| <u>Surfactant</u> | <u>Surface Tension (mN/m)</u> | <u>Spread Diameter (mm)</u> |                |
|-------------------|-------------------------------|-----------------------------|----------------|
|                   |                               | <u>0.1 wt%</u>              | <u>0.2 wt%</u> |
| MSIL-1            | 21.1                          | 27                          | 34             |

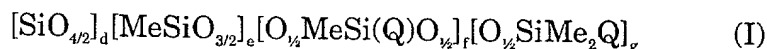
a. Surface tension in mN/m at 25°C.

b. Surface tension of water from CRC Handbook of Chemistry and Physics; 63 Edition, 1982-1983.

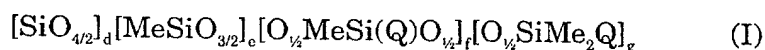
\* Spread diameter of distilled water = 4 mm

We claim:

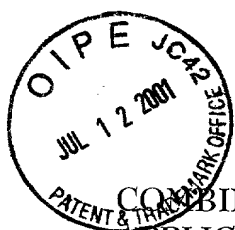
1. A modified organosiloxanes of the present invention have the average general formula:



- 5 wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an amino alkoxyate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging group of C1 to C8, each optionally OH substituted, z = 0 to 1, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R<sup>2</sup> is either a polyether of the structure -BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>c</sub>R<sup>1</sup>, hydrogen or an alkyl radical containing 1 to 18 carbons, c = 0 to 15, and T is a univalent organic moiety.
- 10 2. A composition according to claim 1 wherein T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, -BNR<sup>1</sup><sub>2</sub>, or B-N-B-(SiO<sub>1/2</sub>R<sup>6</sup>)-X<sup>1</sup> wherein X<sup>1</sup> is a siloxane per formula I and R<sup>6</sup> is O<sub>1/2</sub> or -CH<sub>3</sub>.
3. A composition according to claim 1 wherein f = 1 to 5, d = 0, e = 0 and g = 2.
- 20 4. A composition according to claim 1 additionally comprising a pesticide.
5. A composition according to claim 3 wherein T is an alkyl and z = 1.
6. A process for applying a pesticide comprising applying to an animal or plant a composition comprising:



- wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic, g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an
- 5 amino alkoxylate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging group of C1 to C8, each optionally OH substituted, z = 0 to 1, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R<sup>2</sup> is either a polyether of the structure -BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>, hydrogen or an alkyl radical containing 1 to 18 carbons and T is
- 10 a univalent organic moiety.
7. A process according to claim 6 additionally comprising applying a cosurfactant.
8. A process according to claim 6 wherein f = 1 to 5, d = 0, e = 0 and g = 2 and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an
- 15 alkyl amine functionality, -BNR<sup>1</sup><sub>2</sub>, or B-N-B-(SiO<sub>1/2</sub>R<sup>6</sup>)-X<sup>1</sup> wherein X<sup>1</sup> is a siloxane per formula I and R<sup>6</sup> is O<sub>1/2</sub> or -CH<sub>3</sub>.
9. An amine of the formula B'N[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> wherein B' is an alkenyl, with an α, β unsaturation at the end of the alkenyl opposite from the nitrogen atom, a = 2 to 4, b = 2 to 15, z = 1 to 2, B is a divalent bridging group of C1 to C8,
- 20 each optionally OH substituted, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, or -BNR<sup>1</sup><sub>2</sub>.
10. An amie according to claim 9 wherein z = 0.



COMBINED DECLARATION FOR PATENT  
APPLICATION AND POWER OF ATTORNEY

Atty Docket No. SIL-0034 (14283)

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(Includes Reference to PCT International  
Applications)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the invention entitled:

"ORGANOSILOXANE CONTAINING  
MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS"

which is described and claimed in the patent specification which

( ) is attached hereto,

(X) was filed on September 28, 1999 and accorded serial number 09/806,209, and for which  
invention Letters Patent are sought.

I hereby state that I have reviewed and understand the contents of the above identified  
specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this  
application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any  
foreign application(s) for patent or inventor's certificate listed below and have also identified below any  
foreign application for patent or inventor's certificate having a filing date before that of the application  
on which priority is claimed:

| PRIOR FOREIGN/PCT APPLICATIONS AND PRIORITY CLAIMS UNDER 35 U.S.C. 119 |                 |                                    |                     |
|--|-----------------|------------------------------------|---------------------|
| COUNTRY<br>(if PCT, indicate "pct")                                    | APPLICATION NO. | DATE OF FILING<br>(month,day,year) | PRIORITY<br>CLAIMED |
|  |                 |                                    |                     |
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Applications)

I hereby claim the benefit under Title 35, United States Code, Sec.120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec.112, I acknowledge the duty to disclose material information as defined in Title 37, Code Federal Regulation Sec.1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

| PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S.<br>FOR BENEFIT UNDER 35 U.S.C. 120 |                    |                                     |         |           |
|---|--------------------|-------------------------------------|---------|-----------|
| U.S. APPLICATIONS   |                    | STATUS (CHECK ONE)                  |         |           |
| US APPLN. NO.   | US FILING DATE     | PATENTED                            | PENDING | ABANDONED |
| 60/102,039  | September 28, 1998 |                                     |         | X         |
| PCT APPLICATIONS DESIGNATING THE U.S.   |                    |                                     |         |           |
| PCT APPLICATION NO.   | PCT FILING DATE    | US SERIAL NOS.<br>ASSIGNED (if any) |         |           |
| PCT/US99/22490  | Sept. 27, 1999     | 09/806,209                          |         |           |

I hereby appoint the following attorney's and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Kenneth D. Tremain - Reg. No. 20,518; and Daniel Reitenbach - Reg. No. 30,970.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

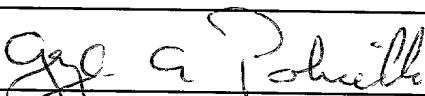


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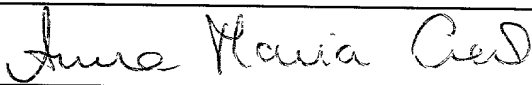
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